



# Mutual promotion by structural design and intrinsic activity coupling of CNTs/MoC/CoNiMo for water splitting and urea electrolysis

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## ABSTRACT

Construction of durable multi-function electrocatalysts for hydrogen production is still highly challenging. Herein, we report a hierarchical integrated tri-functional heterogeneous CNTs/MoC/CoNiMo electrode for HER and related OER/UOR. The carbon-protected Ni nanoparticles yield abundant  $\gamma$ -NiOOH active intermediates to boost OER/UOR, while DFT calculations verify Mo migration induced by MoC and CoNiMo alloy under negative potentials generates HER super-active sites on Mo-rich surfaces. Additionally, the parallel aligned nanosheets with out-plane extended CNTs arrays can guide the rapid bubbles release and expand the accessible surface area. Therefore, the optimized CNT/MoC/NMC-3 electrode can achieve overpotentials of 51 mV (HER) and 226 mV (OER), with low potential threshold of 1.257 V (UOR) at 10 mA cm<sup>-2</sup>. Moreover, the assembled symmetric urea electrolyzer reaches a 1.291 V cell voltage at 10 mA cm<sup>-2</sup>. This work provides a novel strategy for heterostructure multi-component integration for achieving high-efficiency hydrogen production and urea-containing wastewater purification.

## 1. Introduction

Hydrogen with high energy density and pollution-free nature is considered as the most potential alternative sustainable energy to alleviate the energy crisis and environmental pollution [1]. Water electrolysis driven by renewable energy is an economical route with zero-carbon-emission conversion [2]. However, a considerable overpotential is generally required in practical applications of hydrogen production due to the sluggish four-electron anodic oxygen evolution reaction (OER) kinetics. Therefore, the design of the efficient electrocatalysts is still challenging to achieve high electrocatalytic activity and durability.

To address the bottleneck, the development of electrocatalysts with low activation energy barriers, accelerated reaction kinetics, robust structural stability and sufficient exposed active sites is essential [3,4]. Generally, noble metals such as Pt- and Ru/Ir-based compounds exhibit the first-rate activities towards hydrogen evolution reaction (HER) and OER, respectively, but the scarcity and high price have limited their

practical application. Therefore, developing cost-effective electrocatalysts with comparable activity or lower noble metal content becomes highly imperative [5–10]. Recently, transition-metal based alloys and their compounds with non-metallic elements have been widely investigated due to the balanced electronic structure and synergistically-enhanced reaction kinetics in water splitting [11,12]. Wu *et al.* demonstrate a heterogeneous Ni-MoN electrocatalyst consisting metallic Ni and MoN nanoparticles on amorphous MoN nanorods, which can achieve remarkable HER performance with ultralow overpotentials of 61 mV and 136 mV to drive 100 mA cm<sup>-2</sup> and 1000 mA cm<sup>-2</sup>, respectively [13]. Furthermore, constructing ordered and stable micro-structures is another keypoint to promote electrolyte infiltration and gas release [14], which can reduce the “dead volume” and increase the accessible active site density [15]. Zhang *et al.* synthesized a 3D core-shell electrocatalyst consisting of Co(OH)<sub>2</sub> cavity array-encapsulated NiMo alloy on carbon cloth. Benefiting from the open porous structure of the outer Co(OH)<sub>2</sub> array and the multiple active sites at Co(OH)<sub>2</sub>/NiMo heterogeneous interface, the electrocatalyst

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delivers a low cell voltage of 1.52 V at 10 mA cm<sup>-2</sup> in overall water splitting [16].

In addition, the optimization of electrolysis system is another key factor to raise the hydrogen production efficiency and reduce energy consumption [17]. Recently, replacement of the anodic OER process with more readily oxidizable substances including methanol [18], urea [19,20], hydrazine [21], etc., can reduce the thermodynamic voltage required and accelerate reaction kinetics. Among them, urea oxidation reaction (UOR) with low theoretical potential of 0.37 V is attractive process comparing with that of OER (1.23 V vs. RHE). This is especially significant because urea is a potentially free source derived from human urine and urea-rich agricultural wastewater [22,23], which further emphasize the significant potential of UOR process to lower hydrogen production costs and enhance environmental friendliness of the integrated electrocatalytic system [24]. The use of urea thus combines environmental benefits with cost-efficiency. However, UOR is intrinsically sluggish due to the six-electron transfer process. Nickel-based catalysts have been studied as alternatives to noble metals for UOR. Jia *et al.* synthesized an electrocatalyst composed of amorphous Ni(OH)S nanosheets with Ni<sup>3+</sup>-rich phases, which can accelerate the reaction kinetics. The electrocatalyst can achieve low overpotentials of 250 mV and 110 mV toward the OER and UOR at 10 mA cm<sup>-2</sup> [25]. Nonetheless, there is still a challenge to produce multi-component Ni-based electrocatalysts with enhanced reaction kinetics and well-designed 3D nanostructure to achieve high-performance HER and UOR/OER.

Herein, an in-situ growth strategy of CNTs arrays on the parallel aligned NiMoO<sub>4</sub> precursors is reported by one-step chemical vapor deposition (CVD) method, the programmed annealing treatment process enables the preparation of this tightly integrated hierarchical CNTs/MoC/CoNiMo alloy (CNT/MoC/NMC) heterostructure. The active phases evolution and mutual activity coupling under various potentials during electrocatalysis are monitored by ex-situ and in-situ techniques. The Ni nanoparticles with the protective graphite carbon coating possesses great activity and stability, which can accelerate the  $\gamma$ -NiOOH active intermediate formation and stably drive the OER/UOR. DFT calculations have confirmed that MoC and CoNiMo alloy can induce the Mo elements migration to the outer surface under negative potentials, resulting in thermodynamically stable and HER active Mo-surf.-rich surface with an energy difference at least 1.1 eV lower than other systems. Moreover, the out-plane extended CNTs and parallel aligned nanosheets structure can expand the accessible surface area and accelerate the rapidly bubbles release. Therefore, the optimized CNT/MoC/NMC-3 electrode can achieve low overpotential of 51 mV and 226 mV at 10 mA cm<sup>-2</sup> toward the HER and OER, respectively. In addition, the anodic replacement reaction can achieve an exceptional UOR activity of 1.257 V at 10 mA cm<sup>-2</sup>, which is 0.199 V lower than that of the OER. When assembling CNT/MoC/NMC-3 into a symmetric electrolyzer, the cell voltage reduces to 1.291 V at 10 mA cm<sup>-2</sup> to electrolyze urea and can be driven by a 1.5 V button battery.

## 2. Experimental section

### 2.1. Preparation of NiMoO<sub>4</sub>/CoCH

All the raw materials purchased from Aladdin Co. were used directly without any further purification. The heterostructures of NiMoO<sub>4</sub> nanosheets assembled on Co(CO<sub>3</sub>)<sub>0.5</sub>(OH)•0.11 H<sub>2</sub>O (CoCH) nano-needles were fabricated by a two-step hydrothermal treatment according to our previously reported using conductive carbon cloth as the substrate (denoted as NiMoO<sub>4</sub>/CoCH) [26,27].

### 2.2. Preparation of CNT/MoC/NMC-x

The NiMoO<sub>4</sub>/CoCH precursors catalyzed in-situ growth of nitrogen-doped CNTs were conducted in a tube furnace. Firstly, the NiMoO<sub>4</sub>/CoCH composite was calcinated from room temperature to 450 °C with a

heating rate of 4 °C min<sup>-1</sup> in a H<sub>2</sub>/Ar (10:90) atmosphere and kept for 1.5 h. Then, the pre-reduced composite was heated to 600 °C rapidly within 10 min under the same atmosphere. After that, the Ar was cut off and the H<sub>2</sub>, C<sub>2</sub>H<sub>2</sub>, and NH<sub>3</sub> mixture (1:1:0.5) was injected for different periods (1, 2, 3, 5, and 10 min) under 200 mbar. Finally, the H<sub>2</sub>, C<sub>2</sub>H<sub>2</sub>, and NH<sub>3</sub> was cut off and Ar was injected and cool naturally to room temperature to obtain the CNT/MoC/NMC-x (x = 1, 2, 3, 5, and 10 min).

### 2.3. Preparation of CNT/MoC/NMC-n

The effect of reaction temperature on the catalytic growth of carbon nanotubes was compared. The reaction conditions were consistent with the previous step and the reaction time is 3 min, and set the temperature for the growth of carbon nanotubes as 500, 550, 600, 650, and 700 °C, and denoted it as CNT/MoC/NMC-n (n = 500, 550, 600, 650, and 700 °C).

## 3. Results and discussion

### 3.1. Synthesis and structural characterization

The schematics for the synthesis of the CNT/MoC/NMC composites are shown in Fig. 1a, which include a two-step hydrothermal treatment and CVD process. Firstly, a heterostructure consist of parallel aligned NiMoO<sub>4</sub> nanosheet arrays along the axial direction of the CoCH nano-needle arrays on carbon cloth is fabricated (Fig. S1) [27]. Secondly, through a one-step CVD calcination method, the active metal seeds are formed on the NiMoO<sub>4</sub> precursor and the CNTs arrays are catalytic grown on the out-plane of the nanosheets. Fig. 1b illustrates the schematic diagram of the surface restructuring and CNTs growth process of the NiMoO<sub>4</sub> nanosheet. The Ni atoms can be extruded from NiMoO<sub>4</sub> host lattice under thermal-activation and reduction environment, thus form the dispersed Ni nanoparticles and MoO<sub>2</sub> on the surface. Then, after rise the temperature to 600 °C and the introduction of reaction gases, the Ni seeds and active metal species can directly decompose C<sub>2</sub>H<sub>2</sub> to grow CNTs and encapsulated carbon layers. The H<sub>2</sub> and NH<sub>3</sub> can provide reduction atmosphere and nitrogen source to increase the crystallinity and produce more defects and electronic dislocations, which can increase the intrinsic electron conductivity, as well as significantly improves the surface hydrophilicity to facilitate the electrolyte infiltration and active sites exposure. Meanwhile, the MoO<sub>2</sub> can be carbonized to MoC under the relatively low temperature (Table S1). This may be attributed to the high catalytic cracking reactivity of the well-dispersed ultrasmall Ni nanoparticles reduced from NiMoO<sub>4</sub> nanosheets, confirming the advantageous of continuous reaction process in which such seed crystals are in-situ generated from the substrate. Moreover, the CoCH together with NiMoO<sub>4</sub> can form tri-metallic alloy, which enables uniform dispersion of the surface-loaded MoC and CNTs. In the fabrication process, the crystal seeds in-situ generated from the substrate with continuous reaction process is extremely advantageous to evolve heterogeneous structure with tightly interface [28]. In addition, the low-pressure reaction can effectively accelerate the mass transfer between carbonaceous species and metallic catalytic sites for rapid CNTs growth, thus eliminating the potential risk of structural deformation caused by prolonged exposure under high temperature.

X-ray diffraction (XRD) is applied to provide the crystalline evolution process. As shown in Fig. 1c, the peaks belonging to the NiMoO<sub>4</sub> and CoCH disappear after reduction by H<sub>2</sub> (Fig. S2), while the presence of new peaks located at 44.5°, 51.9°, and 76.4° correspond to the metallic Ni (JCPDS 87-0712). Moreover, the peaks located at 37.0° and 41.4° are attributed to the (-211) and (210) planes of MoO<sub>2</sub> (JCPDS 32-0671), while the peaks shift to 36.8°, 39.3°, and 61.5° when reaction is extended to 3 or 5 min, which corresponds to the (006), (103), and (110) planes of MoC (JCPDS 08-0384). Furthermore, within 1 min reaction, the wide peak near 43° may be attributed to the mixed peak of metallic Ni and the tri-metallic alloy of Co<sub>1.3</sub>Ni<sub>4.1</sub>Mo<sub>4.6</sub> with low crystallinity

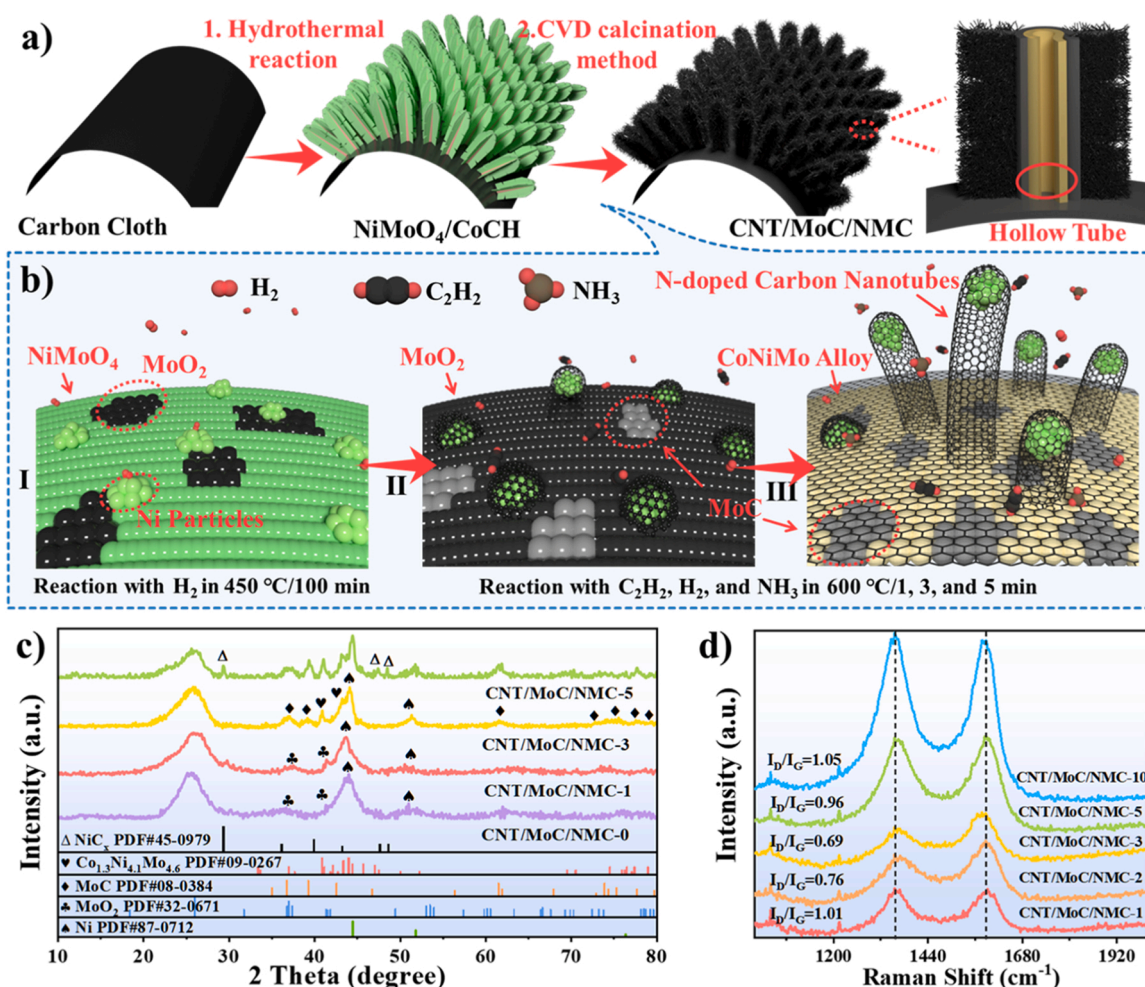


Fig. 1. (a) Schematic illustration of the synthesis process of CNT/MoC/NMC. (b) Schematic diagram of surface reconstruction and CNTs growth during CVD process. (c) XRD patterns and (d) Raman spectra of the CNT/MoC/CoCH-x composites.

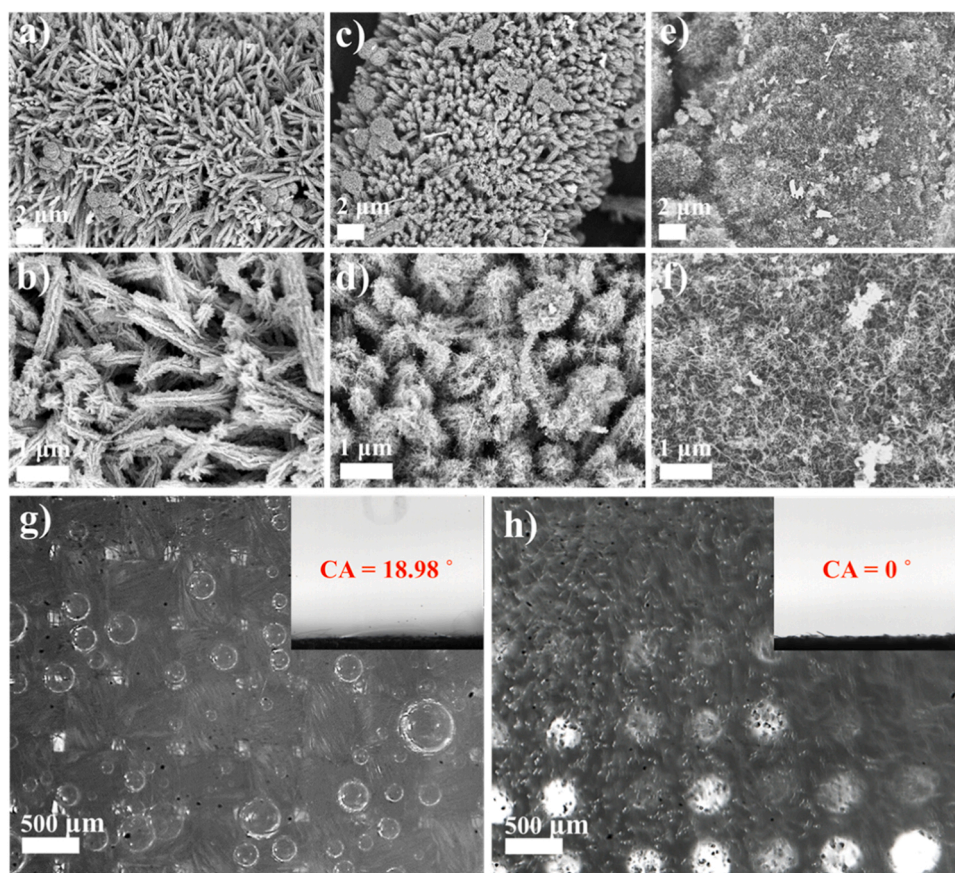
(JCPDS 09-0267). With the extension of treatment time, the peaks centered at  $40.9^\circ$  and  $43.4^\circ$  belongs to  $\text{Co}_{1.3}\text{Ni}_{4.1}\text{Mo}_{4.6}$  appear. The tri-metallic alloy possesses good electrical conductivity, and can form Co- and Mo-doped NiOOH intermediate with high electrocatalysis activity in alkaline solution [29]. Meanwhile, the peaks located at  $29.4^\circ$ ,  $47.7^\circ$ , and  $48.6^\circ$  of CNT/MoC/NMC-5 correspond to the signal of  $\text{NiC}_x$  (JCPDS 45-0979). Furthermore, the graphitization degree of the CNTs and carbon coating is evaluated by Raman spectroscopy. The calculated  $I_D/I_G$  values of the CNT/MoC/NMC-1, 2, 3, 5, and 10 are 1.01, 0.76, 0.69, 0.96, and 1.05 (Fig. 1d), respectively, thus the reaction period of 3 min leads to a higher graphitization degree. Too short growth time is not enough for the orderly extension of CNTs arrays, while too long period may accumulate amorphous carbon on the CNTs surface.

The surface reconstruction and structural evolution is investigated by scanning electron microscopy (SEM). After calcined under  $450^\circ\text{C}$ , the long-range quasi-two-dimensional morphology remains unchanged (Fig. S3), indicating the robust thermostability of the hierarchical heterostructure. Moreover, massive nanoparticles can be observed on the composite surface (Fig. S3f) with obviously magnetic nature after  $\text{H}_2$  reduction (Video S1), verifying the formation of tri-metallic alloy and monodispersed Ni nanoparticles. The effect of reaction time to the CNTs length and composite morphology is also evaluated (Fig. 2 and S4). Within 2 min, the CNTs are inconspicuous and unevenly distributed on nanosheet surface. When growth more than 5 min, the parallel aligned precursor structure is completely disappeared, which significantly reduces the spatial utilization and increases amorphous carbon

accumulation. After 3 min growth, the vertically and densely distributed CNTs arrays on MoC/NMC can be observed, which can effectively promote the electrolyte infiltration, enlarge accessible surface area and build multi-dimensional electron transfer network. In addition, benefiting from the superhydrophilic nature of the surface caused by nitrogen doping, the out-plane extended CNTs arrays can guide the rapid release of the generated gas bubbles and enhance the re-exposure of electrocatalytic active sites. This can be confirmed by its noticeably smaller and uniform dispersed bubbles generated under high current density of  $200\text{ mA cm}^{-2}$  compared to the unloaded CNTs sample, as well as the smaller water contact angle. (Fig. 2g, h, see Video S2 for dynamic details). Accordingly, the corresponding EDS mapping shows the uniform distribution of the elements along the carbon fiber (Fig. S5).

Transmission electron microscopy (TEM) is utilized to investigate the multi-component structure of CNT/MoC/NMC-3 composite. The average CNTs diameter is about 15 nm with Ni nanoparticles encapsulated on the top (Fig. 3a, b). Moreover, due to the reduction under high temperature, the CoCH is decomposed to release  $\text{H}_2\text{O}$  and  $\text{CO}_2$ , while thermally-driven outward migration and eutectic with Ni and Mo species on the surface to form a hollow tri-metallic alloy. Moreover, the hollow structure can enlarge the available electrochemical active area (Fig. S6), thus accelerate active intermediates formation in the electrocatalytic process [30]. The lattice fringes with interplanar spacings of 0.232, 0.209, and 0.218 nm are detected (Fig. 3c), which belong to metallic Ni, MoC, and  $\text{Co}_{1.3}\text{Ni}_{4.1}\text{Mo}_{4.6}$ , respectively. Meanwhile, the heterogeneous structure of coexisted multicomponent can also be





**Fig. 2.** SEM images of the (a, b) CNT/MoC/NMC-1, (c, d) CNT/MoC/NMC-3, and (e, f) CNT/MoC/NMC-5, optical images of the bubble release and related water contact angles (illustration in top right corner) of the (g) NiMoO<sub>4</sub>/CoCH and (h) CNT/MoC/NMC-3 composites.

verified by various detailed surface crystalline and elemental distribution mapping/line scan (Fig. 3i, S7, and S8). The selected area electron diffraction (SAED) patterns also confirm the existence of these three phases (Fig. 3g, h). Furthermore, the corresponding fast Fourier transform (FFT) and inverse FFT patterns of the selected areas contain abundant edge dislocations and lattice distortions (Fig. 3c, e, and f). These defects can provide numerous electrocatalytic active sites whereas avoiding the aggregation of supported nanoparticles [31], thus revealing the strongly coupled heterointerfaces between species. The metallic Ni nanoparticles exhibit excellent crystallinity due to the high temperature treatment, as evidenced by the corresponding FFT pattern in Fig. 3c. In addition, the Ni particles inside the CNTs exhibit a crystal spacing of 0.203 nm, corresponding to the (111) plane of metallic nickel (Fig. 3d). While the interplanar spacing of 0.341 nm belongs to the graphitic carbon, verifying that the Ni nanoparticles are encapsulated by the graphitic carbon layer with a thickness of 1–2 nm. The intimate and ultrathin encapsulation of well-graphitized carbon can not only enhance the structural stability and electrical conductivity, but also profit from the spillover effect of heterogeneous catalysts, thus this “core-shell” structure can modify the number of active sites on the graphitized carbon surface [32,33].

### 3.2. Electrochemical properties

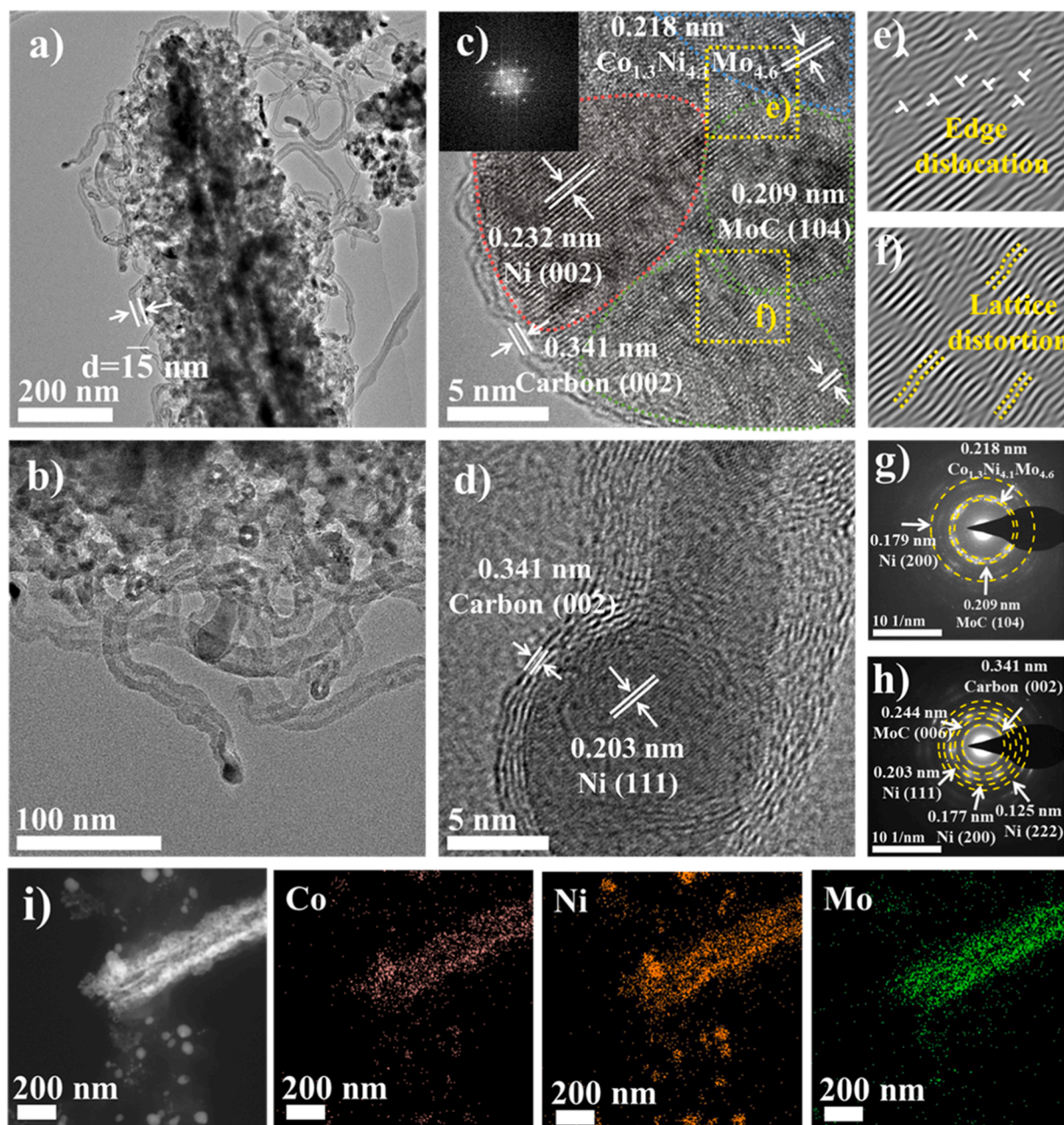
#### 3.2.1. HER and OER catalytic performance

To investigate the HER activities of the electrocatalysts, the linear sweep voltammetry (LSV) curves are tested at 2 mV s<sup>-1</sup> with *iR* correction. The NiMoO<sub>4</sub>/CoCH exhibits an overpotential of 317 mV for HER at 10 mA cm<sup>-2</sup> (Fig. 4a), while the composites exhibit enhanced electrocatalytic ability with overpotentials of 189, 89, 51, 122, and 141 mV at

10 mA cm<sup>-2</sup> for CNT/MoC/NMC-1, CNT/MoC/NMC-2, CNT/MoC/NMC-3, CNT/MoC/NMC-5, and CNT/MoC/NMC-10, respectively. Especially, the optimized CNT/MoC/NMC-3 reveals superior electroactivity with an overpotential of 140 mV under 200 mA cm<sup>-2</sup>, even better than that of the commercial Pt/C (192 mV). The Tafel slope of the CNT/MoC/NMC-3 is calculated to be 66.08 mV dec<sup>-1</sup> (Fig. 4b), which is lower than NiMoO<sub>4</sub>/CoCH (120.65 mV dec<sup>-1</sup>) and other CNT/MoC/NMC-*x* electrodes. Furthermore, the electrochemical active surface areas (ECSA) are determined by calculating the double-layer capacitance (*C*<sub>dl</sub>, Fig. 4g, S9, and S10). The *C*<sub>dl</sub> value increases significantly from 3.93 mF cm<sup>-2</sup> of NiMoO<sub>4</sub>/CoCH to 55.63 mF cm<sup>-2</sup> of CNT/MoC/NMC-3, indicating the large accessible surface area due to the multi-component interfaces and the extended CNTs arrays. The superior HER activity may benefit from the accelerated reaction kinetics of well-designed MoC and CoNiMo alloy in alkaline solution, while the hierarchical heterostructure and well-distributed active species can promote the electrolyte infiltration and intrinsic activity. Moreover, the uniform CNTs can effectively separate the generated bubbles rapidly and facilitate the re-exposure of the active sites, especially under high current density, thus enhancing the HER stability.

Moreover, as the CNT/MoC/NMC-*x* composites consist of multiple active sites, the OER can be occurred rapidly driven by the coupled active components. As shown in Fig. 4d, the optimal CNT/MoC/NMC-3 electrode reveals a relatively low overpotential of 226 mV at 10 mA cm<sup>-2</sup> for OER, which is superior than the benchmark IrO<sub>2</sub> catalyst (243 mV). A clear oxidation peak can be observed at around 1.3–1.4 V (vs. RHE), which can be ascribed to the oxidation of Ni<sup>0</sup> species in Ni-based catalysts to form NiOOH [34]. In comparison, the oxidation peak of the NiMoO<sub>4</sub>/CoCH precursor is difficult to be distinguished, demonstrating that the highly active metallic Ni inside the





**Fig. 3.** (a–d) TEM images with corresponding FFT patterns (c inset), (e, f) corresponding FFT and inverse FFT of the selected area in (c), (g, h) corresponding SAED patterns and (i) high-resolution elemental mappings of CNT/MoC/NMC-3 composite.

carbon layers can promote the  $\text{OH}^-$  adsorption and OER process [35]. The lowest Tafel slope of  $58.71 \text{ mV dec}^{-1}$  for CNT/MoC/NMC-3 verifies the highest OER reaction kinetics (Fig. 4e).

To further estimate the mass transfer kinetics, the electrochemical impedance spectroscopy (EIS) is measured and fitted by equivalent circuit (Fig. 4c, f). The values of the solution resistance ( $R_s$ ), interface resistance ( $R_p$ ), and charge-transfer resistance ( $R_{ct}$ ) of CNT/MoC/NMC-3 composite are the smallest among all electrodes, which are 2.19, 0.21, and  $1.12 \Omega$  for HER, and 2.26, 0.83, and  $4.81 \Omega$  for OER, respectively (Tables S2 and S3). This result demonstrates the promotion of the mass transfer efficiency by the extension of the encapsulated Ni along with CNTs into the electrolyte and the synergistic effect between multiple dominant components. Additionally, the turnover frequency (TOF) values of the CNT/MoC/NMC-3 are calculated to be  $0.699 \text{ s}^{-1}$  for HER and  $0.937 \text{ s}^{-1}$  for OER (Fig. 4h, S11), respectively, indicating the

superior instantaneous efficiency for water electrolysis. Furthermore, the CNT/MoC/NMC-3 also reveals excellent stability within 40 h long-term catalysis at  $100 \text{ mA cm}^{-2}$  for both HER and OER (Fig. S12). As summarized in Fig. 4i, the theoretical overall overpotentials indicate the lowest overpotential of the CNT/MoC/NMC-3 hybrid (277 mV), suggesting the excellent overall water splitting efficiency of the bifunctional catalyst. Moreover, the two-electrode electrolyzer is assembled by employing CNT/MoC/NMC-3 as both anode and cathode, a low cell voltage of 1.51 V is required to achieve  $10 \text{ mA cm}^{-2}$  (Fig. S13a, b), which is superior than most of the high-end devices (Fig. S14). In addition, the effects of different growth temperatures and carbon sources (methane, melamine, and dicyandiamide) on the morphology and electrocatalytic properties during the CNTs growth process are also investigated, while the results demonstrate the optimal treatment temperature of  $600^\circ\text{C}$  (Figs. S15–19, Tables S4 and S5), and acetylene is

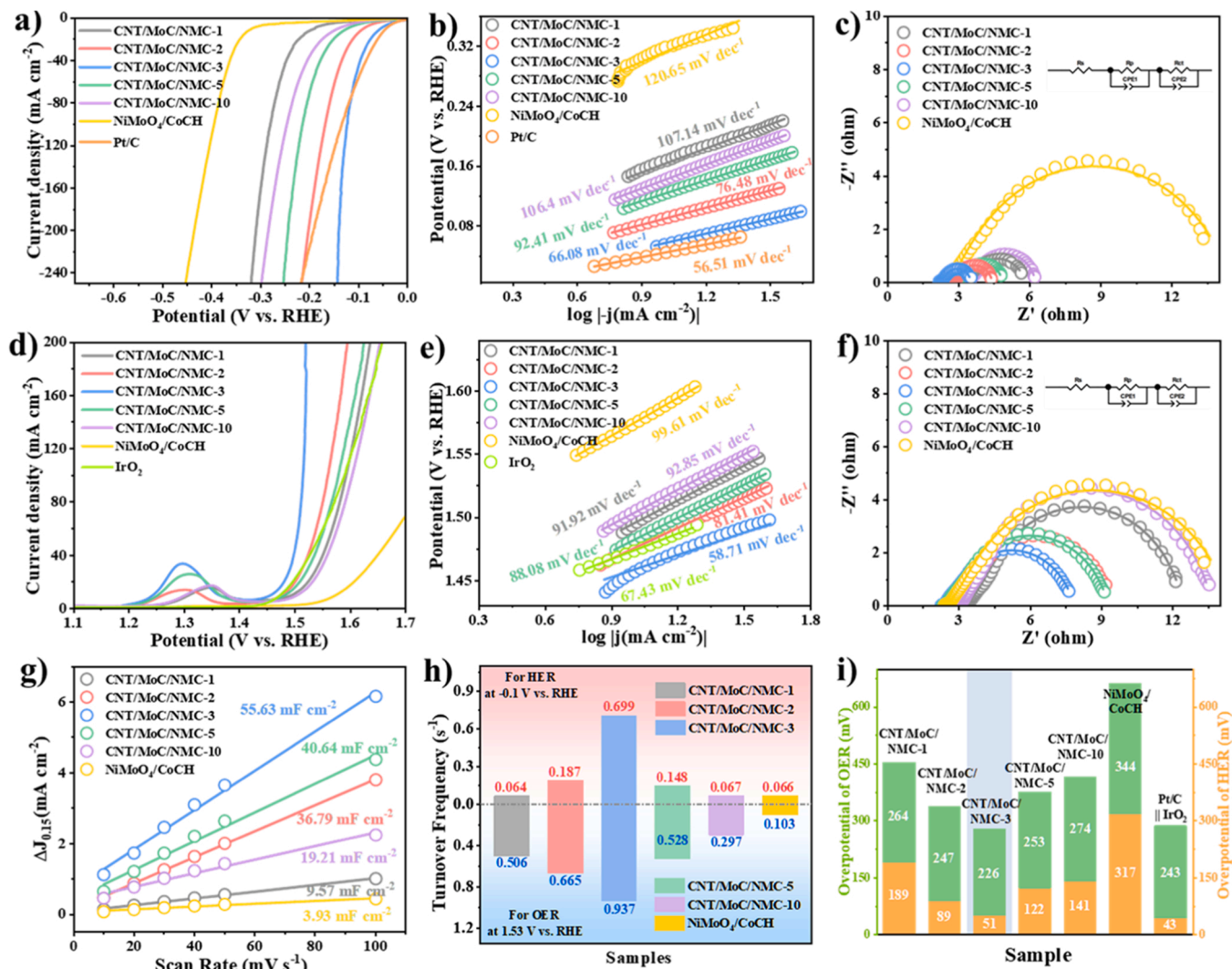


Fig. 4. (a) LSV curves, (b) Tafel plots, (c) Nyquist plots for HER; (d) LSV curves, (e) Tafel plots, (f) Nyquist plots for OER; (g)  $C_{dl}$  values and (h) TOF values of the CNT/MoC/NMC- $x$  and NiMoO<sub>4</sub>/CoCH electrodes; (i) The overall overpotential of the corresponding electrodes obtained at 10 mA cm<sup>-2</sup>.

selected as the best-matched carbon source (Figs. S20–23). The relatively low growth temperature and optimal carbon source are beneficial to maintain the hierarchical nanostructure as well as increase the preparation economy.

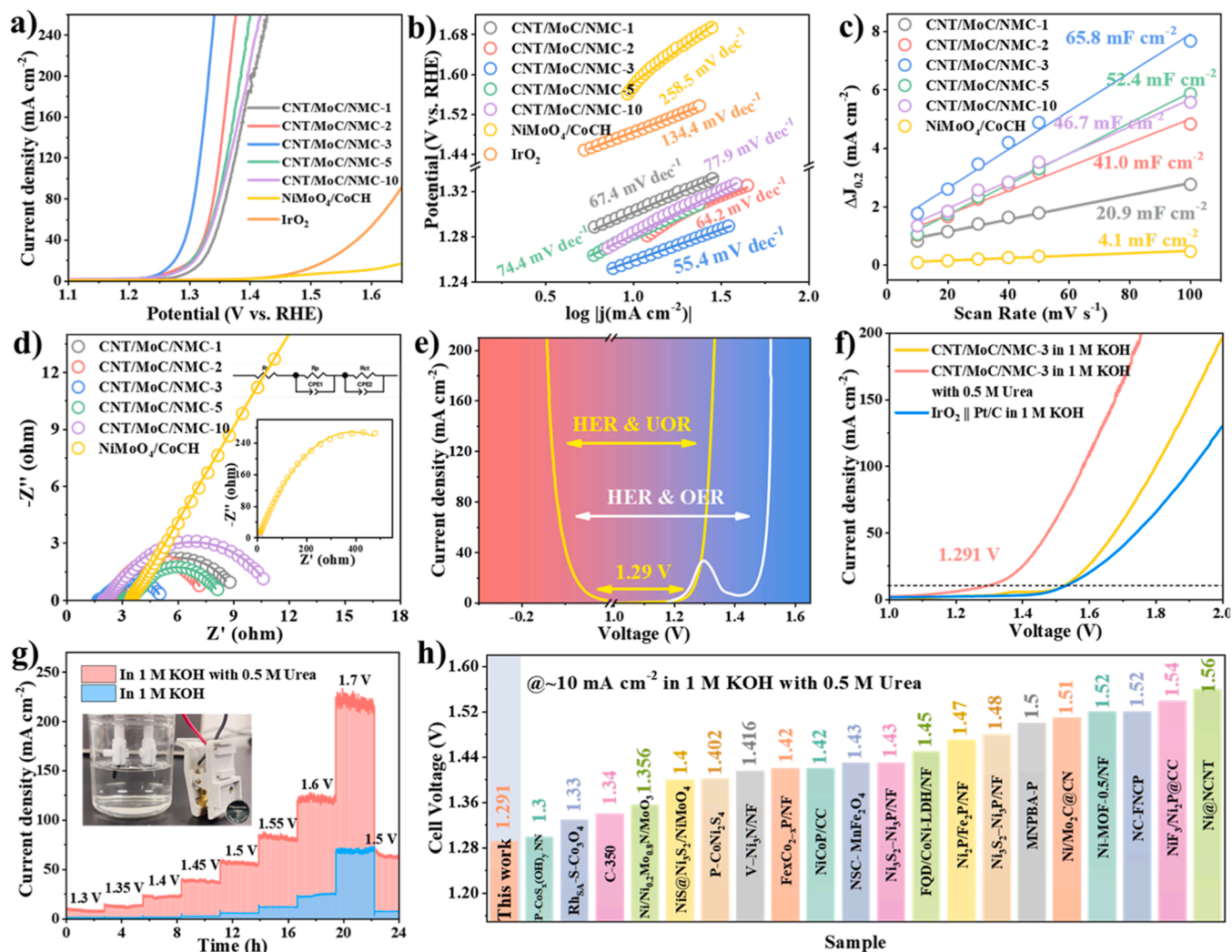
### 3.2.2. UOR and urea electrolysis

In order to decrease the operation potential during H<sub>2</sub> generation, the UOR reaction is further studied to substitute OER process. In three-electrode configuration, the LSV curve of the CNT/MoC/NMC-3 reveals enhanced UOR activity with potential of 1.257 V at 10 mA cm<sup>-2</sup> (Fig. 5a), which is much lower than that of the OER. In addition, varied urea concentrations are investigated, while 0.5 M is demonstrated to be the most appropriate concentration for this system (Fig. S24). Moreover, the oxidation peak position of OER is in line with that of the UOR (Fig. S25), confirming that the encapsulated Ni species are conducive to generate NiOOH and serve as active species for anodic oxidation reaction. In comparison, the NiMoO<sub>4</sub>/CoCH and IrO<sub>2</sub> electrodes reveal no improvement in UOR activity (1.576 V and 1.484 V at 10 mA cm<sup>-2</sup>). Furthermore, the CNT/MoC/NMC-3 exhibits Tafel slope of 55.4 mV dec<sup>-1</sup>, which is considerably lower than 134.4 mV dec<sup>-1</sup> for IrO<sub>2</sub> electrode, indicating the optimal adsorption characteristics and rapid reaction kinetics for the urea molecules (Fig. 5b). The boost UOR activity of the CNT/MoC/NMC-3 can also be proven by the highest  $C_{dl}$  value (65.8 mV cm<sup>-2</sup>, Fig. 5c, S26), the lowest interface resistance and fastest

charge-transfer kinetics (0.41  $\Omega$  of  $R_p$  and 3.06  $\Omega$  of  $R_{ct}$ , Fig. 5d, Table S6), and the superior intrinsic electrocatalytic activity (TOF value of 1.710 s<sup>-1</sup>, Fig. S27). Furthermore, with the absence of CNTs arrays and MoC active substances, both composites reveal inferior electrocatalytic behavior compared with CNT/MoC/NMC-3 (Figs. S28–S34, Tables S7 and S8), verifying the enormous benefits of reasonable structural design and integrated coupling between multiple active components.

To investigate the potential practical application, the CNT/MoC/NMC-3 electrode is assembled to the urea electrolyzer. The LSV curve for HER in urea-containing solution only exhibits a slightly cathodic shift compared with that in pure KOH, suggesting a robust electrocatalytic ability under various conditions (Fig. S35). The theoretical cell voltage of the device at 10 mA cm<sup>-2</sup> is 1.290 V in urea-containing electrolyte, which is 0.22 V lower than that in water electrolysis, indicating an enhanced H<sub>2</sub> production efficiency (Fig. 5e). Specifically, the actual measured cell voltage is 1.291 V (Fig. 5f), which is close to theoretical value and is comparable or better than most of the high-end electrocatalysts (Fig. 5h, Table S9). In addition, the electrolyzer can react steadily under varied constant cell voltage from 1.3 V to 1.7 V for 24 h (Fig. 5g and Fig. S36), while the enlarged current density disparities between urea electrocatalysis and water splitting can be observed with increasing bias voltage, suggesting excellent operation durability and activity. Moreover, the parallel aligned structure with plenty CNTs





**Fig. 5.** (a) LSV curves, (b) Tafel plots, (c)  $C_{dl}$  values, and (d) Nyquist plots of CNT/MoC/NMC- $x$ , NiMoO<sub>4</sub>/CoCH, and IrO<sub>2</sub> electrodes for UOR. (e) Theoretical voltage values of CNT/MoC/NMC-3 toward HER with UOR/OER. (f) LSV curves of CNT/MoC/NMC-3 and Pt/C||IrO<sub>2</sub> systems in various electrolytes. (g) Durability of electrolyzer at various cell voltage, inset: electrolyzer powered by 1.5 V button battery. (h) Comparison of cell voltage required to drive 10 mA cm<sup>-2</sup> of various urea electrolysis catalysts.

remains unchanged under fast surface reaction and bubble disturbance (Fig. S37), verifying the robust structural stability. Considering the portable advantage of devices powered by commercial batteries, the urea electrolysis configuration can be driven by single 1.5 V button battery (Fig. 5g, Video S3). Profiting from the coupling of intrinsic activity and structural superiority between multi-component, urea electrolysis occurs violently and the generated bubbles can be released under guidance of CNTs arrays.

### 3.3. Mechanism analysis of enhanced electrochemical activities

#### 3.3.1. The evolution of electronic structure

To understand the evolution of electronic structure and active intermediates under the applied potential, related ex-situ and in-situ characterizations are performed. The surface valence states of CNT/MoC/NMC-3 before/after UOR is investigated by X-ray photoelectron spectroscopy (XPS, Fig. S38). All the binding energies of metal elements reveal obvious positive shift after long-term UOR operation, reflecting the promotion of corresponding oxidation states. In Ni 2p spectra, the strong peaks located at 853.1 eV and 870.2 eV can be assigned to Ni<sup>0</sup> species (Fig. 6a) [36], which is consistent with massive metallic Ni nanoparticles inside CNTs and on the tri-metallic alloy surface. The

weak peaks centered at 855.6 eV and 873.0 eV belongs to the partially oxidized Ni<sup>2+</sup> species. After urea electrolysis, a pair of new peaks appear at 857.5 eV and 875.6 eV, which are attributed to Ni<sup>3+</sup> [37], while the peaks for metallic Ni disappear. Moreover, the Mo species are completely converted to Mo<sup>6+</sup> under the long-period oxidation conditions (Fig. 6b). In Co 2p spectra, the Co<sup>0</sup> signal also disappears after UOR (Fig. 6c), while the proportion of Co<sup>3+</sup> content increases from 21.26 % to 56.38 %. The significant elevation of the oxidation state of CNT/MoC/NMC-3 after UOR can also be confirmed by XRD and Raman results (Fig. S39).

For O 1s, four peaks located at 530.3, 531.2, 532.1, and 533.4 eV are related to the metal-oxygen, hydroxyl species, oxygen vacancies, and adsorbed oxygen, respectively (Fig. 6d) [38]. The increased O-H content and the appearance of Ni<sup>3+</sup> further imply the formation of nickel oxyhydroxide [39]. The N 1s in Fig. 6e corresponds to the presence of pyridinic N (398.4 eV), pyrrolic N (400.2 eV), and graphitic N (401.8 eV) [35]. The peak located at 394.3 eV is attributed to the Mo 3p [1], where N-Ni/Mo (396.9 eV) [40] is detected due to the bonding of Ni/Mo species with N atoms. The N 1s signal is enhanced significantly after continuous electrolysis, probably resulting from the adsorption and transformation of nitrogen-containing intermediates during UOR process. The accumulation of pyridinic/graphitic N electron-acceptor



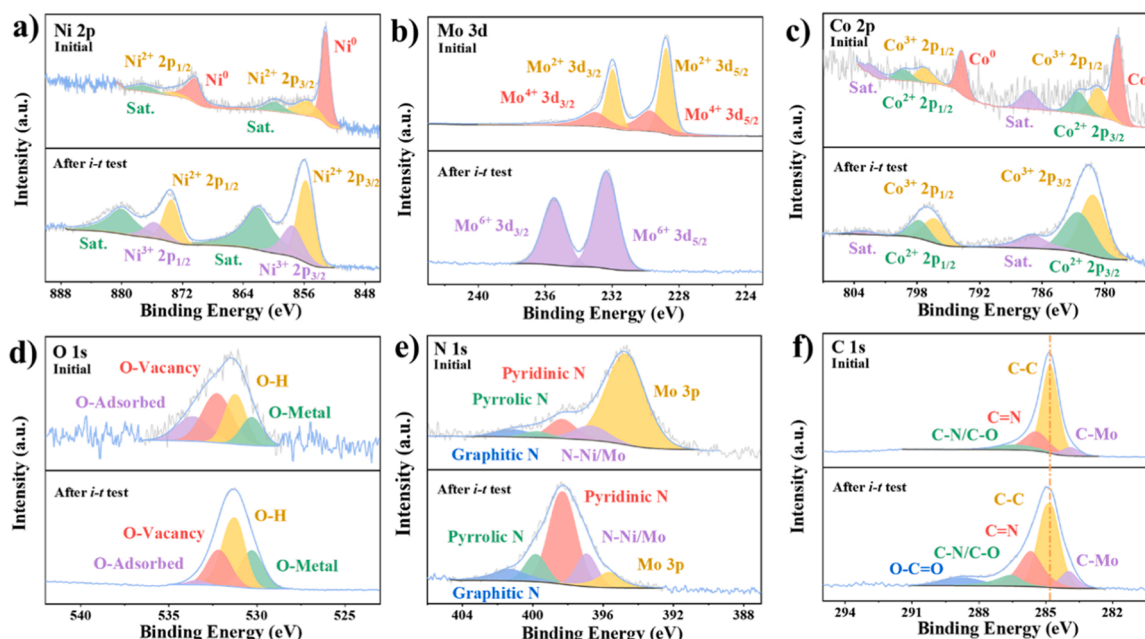


Fig. 6. XPS (a) Ni 2p, (b) Mo 3d, (c) Co 2p, (d) O 1s, (e) N 1s, (f) C 1s spectra of the CNT/MoC/NMC-3 before/after long-term UOR.

potentially generates positive charges on adjacent  $sp^2$ -hybridized carbon atoms, thus accelerate the intrinsic reaction kinetics [41]. The binding energies of C 1s at 283.9, 284.8, 285.4, and 286.3 eV are in accordance with the C-Mo, C-C, C=N, and C-N/C-O (Fig. 6f) [42]. Identification of C-N and C=N bonds confirms the entrance of N atoms into the carbon skeleton and stimulates chemical interactions with adjacent metal/carbon atoms, which can generate structural defects in CNTs to generate activated chemisorption sites [35]. After urea electrolysis, the appearance of the O-C=O bond located at 289.3 eV attaches to the interaction of carbonate anions in electrolyte into the carbon interlayer [43].

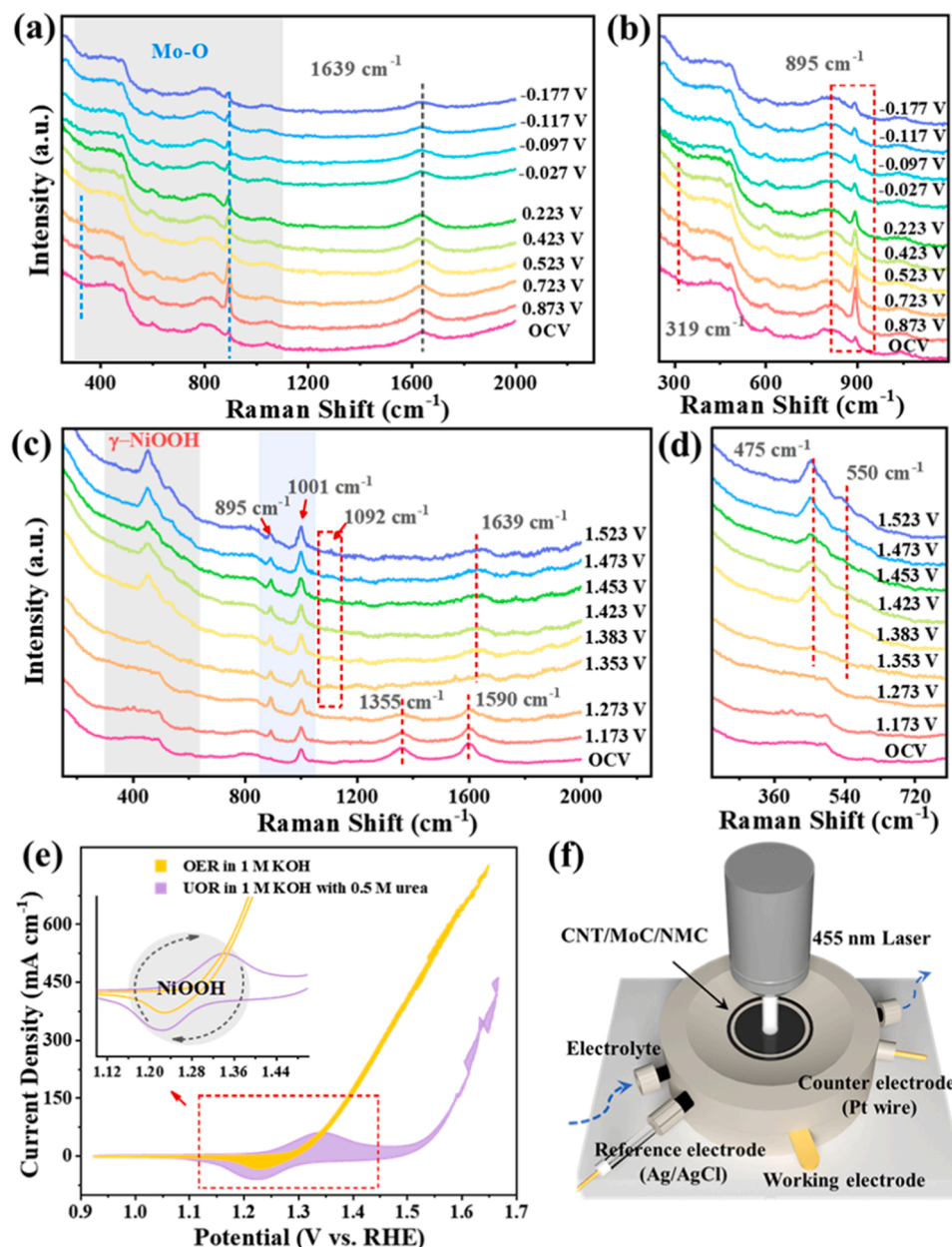
### 3.3.2. The evolution of active intermediates

To further identify the surface states of multi-components heterostructure, in-situ Raman spectroscopy is employed to clarify the real-time intermediates evolution of CNT/MoC/NMC-3 electrode. The varied applied potentials are compensated by solution resistance to eliminate the influence of different device configuration (Fig. S40). Moreover, with the addition of electrolyte, a peak belonging to the O-H stretching of water appears at  $1639\text{ cm}^{-1}$  (Fig. S41). For HER, two peaks around  $319\text{ cm}^{-1}$  and  $895\text{ cm}^{-1}$  emerge at 0.873 V (vs. RHE, Fig. 7a, b), indicating the transformation of low-valent Mo species to  $\text{Mo}^{6+}\text{-O}$  in the multi-component catalysts after activation [44]. With increasing negative potentials, a gradual weakening of peak signals is observed until hydrogen evolution occurs entirely at  $-0.027\text{ V}$ . The dynamic evolving behavior of Mo component at reductive potentials is revealed by the coordination of hexagonal MoC with CoNiMo alloy during HER (more details are provided in DFT calculations below). In comparison, the  $\text{NiMoO}_4/\text{CoCH}$  precursor reveals three peaks, the two located at  $339\text{ cm}^{-1}$  and  $838\text{ cm}^{-1}$  belong to  $\text{MoO}_4^{2-}$  vibrations, while the sharp peak at  $927\text{ cm}^{-1}$  can be assigned to symmetric stretching of Ni-O-Mo (Fig. S42) [45,46]. These peaks are significantly strengthened with the increase of applied potential, suggesting the HER reaction occurs at intrinsically inert  $\text{NiMoO}_4$  sites due to the relatively negative Gibbs free energies of  $\text{H}^+$  [47]. Thus, the optimized electronic structure can balance hydrogen adsorption/desorption and lead to synergistically-enhanced HER kinetics [48,49]. In addition, the surface evolution of CNT/MoC/NMC-3 for HER in urea-alkaline electrolyte is also explored, though some of the signals are influenced by the urea, the variation trend is consistent with the activity mechanism in pure KOH

electrolyte (Fig. S43).

For UOR process, a peak appears at  $1001\text{ cm}^{-1}$  when no bias voltage is applied (Fig. 7c, d), which is attributed to symmetric C-N stretch of urea molecules attached onto carbon surface [50]. Besides, the peak at  $1092\text{ cm}^{-1}$  is assigned to the symmetric stretch of  $\text{CO}_3^{2-}$ , which is one of the products in UOR [51]. A pair of D and G peaks can be noticed, which may due to synergistically enhancement of urea molecules to graphite carbon (Fig. S43). The D and G bands disappear when the applied potential reaches 1.353 V, and is reversible after CV cycling (Fig. S44). The doublet peaks of  $\gamma\text{-NiOOH}$  located at  $475\text{ cm}^{-1}$  and  $550\text{ cm}^{-1}$  emerge at 1.353 V [52], indicating the partial reconstruction of massive metallic Ni particles inside carbon layers, a diffraction peak attributed to  $\text{NiC}_x$  can be detected in the post-electrolysis XRD pattern (Fig. S39a), verifying the long-term continuous mass transfer of the activated Ni particles to the electrolyte during UOR. In addition, transient evolution of the  $\gamma\text{-NiOOH}$  intermediate can also be observed in OER process of CNT/MoC/NMC-3 (Fig. S45). The activation of Ni nanoparticles during anodic oxidation can also be demonstrated by evolving potential of Ni-based intermediates, corresponding to the clear redox peaks in CV curve due to the Faraday process of Ni (III) conversion (Fig. 7e). The relatively high degradation of catalytic performance in near-neutral electrolyte also confirms that these electrocatalytic active components with positive charges can favorable the surface  $\text{OH}^-$  adsorption kinetics to boost the reaction (Fig. S46). In comparison, the in-situ Raman of  $\text{NiMoO}_4/\text{CoCH}$  in UOR reveals the absence of Ni-based intermediates (Fig. S47), the insufficient active sites produced by  $\text{NiMoO}_4$  may directly consumed by urea [53]. Moreover, due to the chemisorption of OH radicals in alkali electrolyte, a pair of peaks located at  $461\text{ cm}^{-1}$  and  $528\text{ cm}^{-1}$  appear (Fig. S48) [54], which belongs to  $\text{Ni}(\text{OH})_2$  and cannot be transformed into  $\gamma\text{-NiOOH}$ . It is verified that the monoclinic nickel molybdate oxides exhibit limited activity and sluggish reaction kinetics in UOR than in OER (Fig. S49).

Furthermore, DFT calculations are carried out to investigate the mutual coupling and evolution process of active components, specifically CoNiMo and MoC, and the appropriate theoretical models are constructed. Among the three typical geometries of CoNiMo alloy, namely, Mo-bulk-rich, Mo-surf.-rich, and Mo-averaged surfaces, our findings indicate that the Mo-surf.-rich CoNiMo alloy surface exhibits highest thermodynamic stability, with an energy difference of at least 1.1 eV lower than the other systems (Fig. 8a). This particular surface

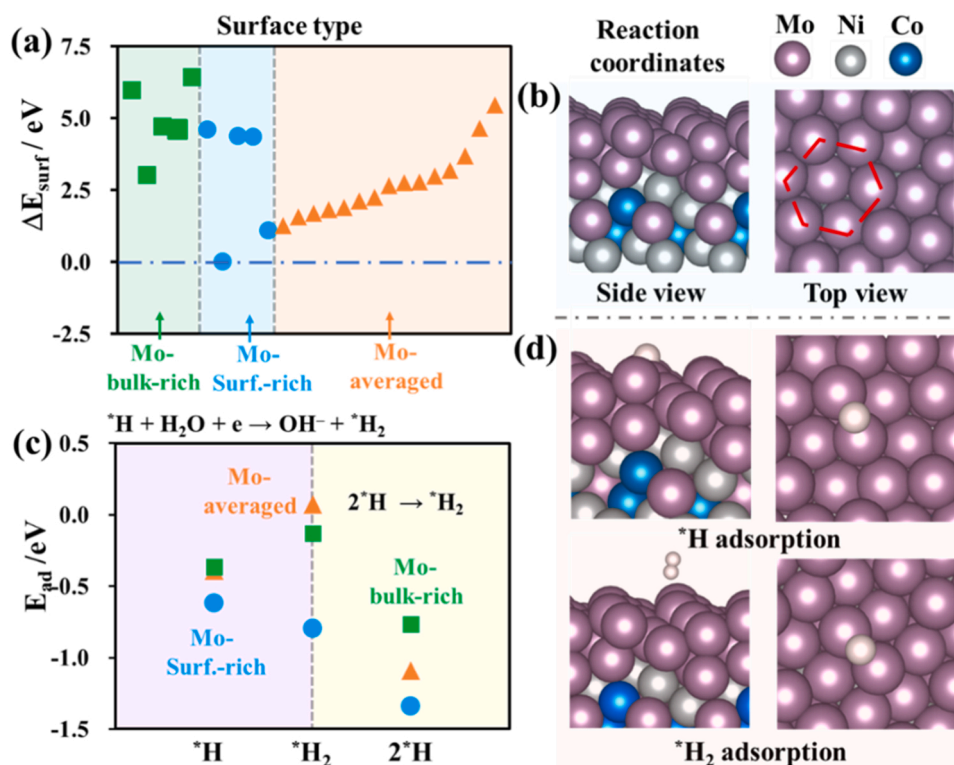


**Fig. 7.** *In-situ* Raman spectra of the CNT/MoC/NMC-3 as a function of applied potential vs. RHE in (a, b) HER and (c, d) UOR. (e) CV curves of the CNT/MoC/NMC-3 at 5 mV s<sup>-1</sup>. (f) Schematic illustration of the *in-situ* Raman cell.

undergoes noticeable surface reconstruction, evidenced by the formation of atom steps, while still maintaining a hexagonal shape with dense packing (Fig. 8b). The reconstruction of the Mo-surf.-rich surface is attributed to the larger radius of Mo (145 pm) compared to Ni and Co (135 pm), which relieves the stress/strain present in the other systems and contributes to its enhanced thermodynamic stability. Moreover, the most stable surfaces among the Mo-bulk-rich, Mo-surf.-rich, and Mo-averaged surface-series are tested as the active sites for the hydrogen evolution reaction. The results, depicted in Fig. 8c, clearly demonstrate that the Mo-surf.-rich surface enables the Heyrovsky step ( $*\text{H} + \text{H}_2\text{O} + \text{e}^- \rightarrow \text{OH}^- + * \text{H}_2$ ) without requiring negative potentials. Conversely, minimum applied potentials of -0.31 V and -0.54 V are necessary for the Mo-averaged surface and Mo-bulk-rich surface, respectively. It is important to note that the Volmer step of  $2\text{H} \rightarrow * \text{H}_2$  cannot occur on CoNiMo alloy surfaces. Therefore, we propose that the Mo-surf.-rich surface represents the super-active site for HER process (Fig. 8d). Regarding the HER on MoC, a negative potential of -0.50 V is required

to facilitate the reaction (Fig. S50).

Therefore, the excellent electrocatalytic performance in HER, OER, and UOR of the CNT/MoC/NMC-3 electrode can be attributed to the following reasons: (1) The parallel nanosheet arrays with densely coated CNTs can significantly enlarge the accessible active area and reduce the steric hindrance of active sites, while the out-plane CNTs arrays can also guide the bubble desorption. (2) *In-situ* growth on NiMoO<sub>4</sub> surface without extra-seeds addition can regulate the morphology of CNTs, together with remarkable activity and stability of the embedded ultra-small Ni nanoparticles under carbon layers protection. (3) The intermediate evolution process in multi-interfacial heterostructures can facilitate the electrocatalytic activity: the coordination of MoC and CoNiMo alloys induce the migration of Mo species to outer surface under negative potentials, resulting in thermodynamically stable Mo-surf.-rich surface preferable for HER; while plenty of metallic Ni nanoparticles wrapped inside carbon layers can evolve into highly active  $\gamma$ -NiOOH sites for UOR and OER. By design the multi-component integrated



**Fig. 8.** CoNiMo as the active sites for HER. (a) The energy difference of the three typical surface series. (b) The side and top view of the reconstructed Mo-surf.-rich surface. (c) The energy diagram of the Herovskey step and Volmer step in HER. (d) Adsorption geometries of  $^*\text{H}$  and  $^*\text{H}_2$ .

heterostructures, it may provide novel idea for the development of industrial hydrogen production in the future.

#### 4. Conclusions

In summary, we report a facile strategy for in-situ construction of integrated hierarchical tri-functional CNTs/MoC/CoNiMo heterostructures, and elucidate the dynamic evolution of multiple components during electrocatalysis. The nickel nanoparticles protected by carbon layers possess superior activity and stability, which can accelerate the formation of  $\gamma\text{-NiOOH}$  active intermediates for OER/UOR. The MoC cooperates with CoNiMo tri-metals can form Mo-surf.-rich surface to strengthen intrinsic activity for HER. Driven by the structural advantages of out-plane extended CNTs and parallel aligned nanosheets, bubbles separation and active intermediate evolution are promoted, ultimately remarkably accelerating the electrocatalytic reaction. Therefore, the optimized CNT/MoC/NMC-3 can achieve low overpotentials of 51 mV and 226 mV at  $10 \text{ mA cm}^{-2}$  for HER and OER, as well as an exceptional potential of 1.257 V to deliver  $10 \text{ mA cm}^{-2}$  for UOR. Furthermore, the assembled symmetric electrolyzer can achieve low cell voltage of 1.291 V at  $10 \text{ mA cm}^{-2}$  for urea electrolysis. This paper integrates the fabrication of high-efficiency catalyst and the optimization of electrolysis system, which offers a promising pathway for achieving hydrogen economy coupled with purification of urea-rich wastewater.

#### Supporting information

Supplementary experimental section, electrochemical tests and related calculation, fitted equivalent circuits, and SEM, EDS, XRD, XPS, Raman tests of the composites are listed in the [Supporting Information](#).

#### CRediT authorship contribution statement

X. L.: Investigation, Experimental, Data analysis, Writing – original draft. K. D.: Data analysis. P. L.: Data analysis, Visualization. X. L.: Data analysis. W. T.: Visualization, Investigation. K. M.: Visualization, Writing – review & editing. H. L.: Theoretical simulation. J. J.: Conceptualization, Investigation, Supervision, Writing – review & editing, Funding acquisition.

#### Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

#### Data Availability

Data will be made available on request.

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#### Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at [doi:10.1016/j.apcatb.2023.123470](https://doi.org/10.1016/j.apcatb.2023.123470).



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